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CHEMICALLY MODIFIED ELECTRODES

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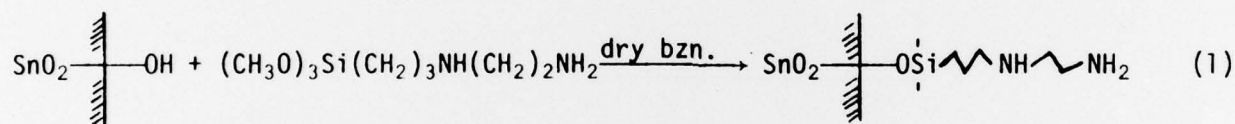
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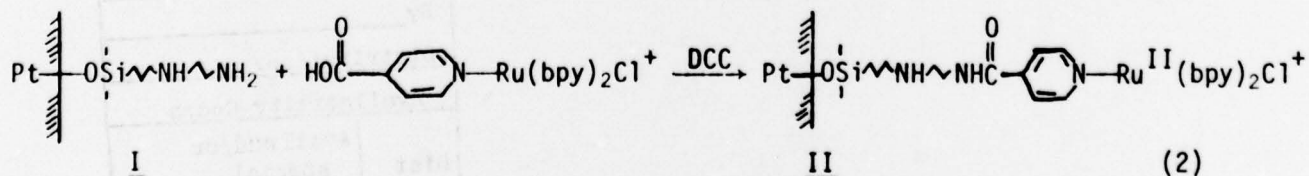
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My colleagues¹ and I ventured into surface synthesis in Spring, 1974. Using X-ray photoelectron spectroscopy (XPS), we demonstrated² the following reaction



The SnO_2 electrode surface was thus functionalized, or "chemically modified", with amine groups and from a synthetic perspective can be considered an "amine surface". This was an important step because now one can rationally plan coupling reactions with the "amine surface", to attach other interesting molecules to it.

Electrochemically reactive molecules are the most interesting candidates to attach to a functionalized electrode surface. For example, ruthenium complexes with peripheral carboxylic acid groups can be amide coupled³ to an alkylamine-silanized Pt oxide⁴ surface.

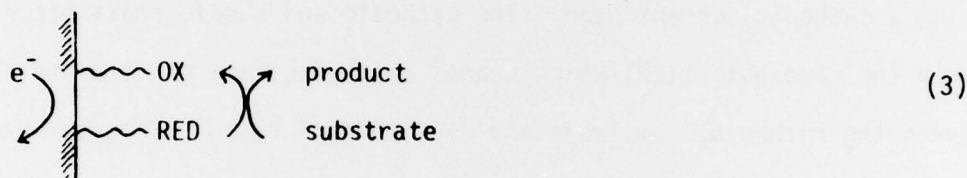


By applying a potential to the Pt electrode II immersed in an electrolyte/solvent medium, the immobilized Ru(II) complex can be made to undergo the same oxidation and reduction reactions it would exhibit if dissolved in solutions of electron acceptor or donor reagents. Thus, sweeping the potential linearly, as in cyclic voltammetry, II becomes oxidized in an anodic current peak at +0.79 volt (Figure 1). The Ru(III) complex product remains attached to the Pt, and is reducible in a reverse potential sweep, giving a cathodic current peak. The cathodic and anodic peaks occur at nearly the same potential, which means⁵ that electrons are transferred between the ruthenium complexes and Pt much more rapidly than the experimental time scale. The immobilized complexes can be exhaustively oxidized and reduced many times, and the quantity of attached complex, or coverage, Γ_{Ru} , is approximately molecular (1.1×10^{-10} mole/cm.², 6.6×10^{13} molecules/cm.², $151 \text{ \AA}^2/\text{molecule}$). These observations are typical of a number of reports of redox species immobilized on electrodes.

Why is it of interest to attach electrochemically reactive molecules to electrodes? First, such molecules should have special characteristics favoring study of intramolecular and electrochemical electron transfers. For example, it is interesting to view the surface "molecule" (Pt lattice)-OSi~Ru(II) in terms of an intramolecular electron exchange in which one end (the Pt) of the "molecule" has a continuously adjustable chemical potential. In semiconductor electrodes, "surface states" are energy levels in the semiconductor band gap whose chemical nature is generally unknown. Deliberate surface attachments offer a means of introducing⁶ surface states of known energy and molecular nature into the band gap. Another feature, with electrochemical kinetic implications, is that no conventional mass transfer of reactant and product to and from the electrode is required for the reaction in Figure 1, since the ruthenium complexes reside already near the plane of space next to the Pt

lattice where electron transfer occurs.

Secondly, there are a number of interesting ways to exploit the chemical and optical as well as electrochemical properties of attached molecules. Thus, electrochemically reactive molecules attached to electrodes can be applied in electrocatalysis. In electrocatalysis, the attached molecule acts as a fast electron transfer mediator⁷ for a substrate dissolved in the contacting solution and only slowly reduced directly by a naked electrode.



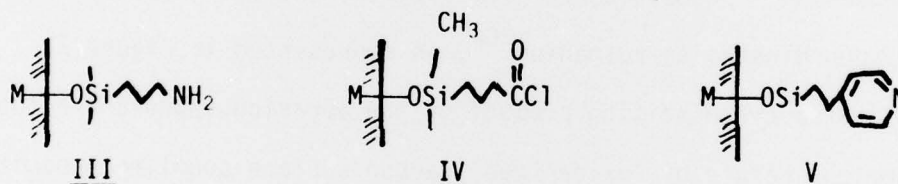
Conceptually the mediation reaction can be either inner or outer sphere. On a semiconductor electrode such electrocatalytic reactions can be incorporated into more complicated photosensitization⁸ and anti(photoanodic)corrosion⁹ schemes. The optical properties of multimolecular layers of redox substances immobilized on transparent electrodes like SnO_2 can also be exploited, to devise potential-switchable colored electrodes¹⁰.

It is evident that a major virtue of the ability to synthetically manipulate the molecular composition of an electrode surface, is that schemes of behavior like the above can be anticipated and then experimentally sought. This is a sharp departure from the traditional Edisonian surface treatment approach used by electrochemists in the course of seeking useful electrochemical behavior of solid electrodes toward reactants dissolved in the contacting solvent. Chemical modification yields a new degree of freedom in electrochemical science. It follows then that an important aspect of modified electrodes is to what extent if any the chemical behavior(s) of molecules are unpredictably altered by immobilization.

HOW TO MAKE MODIFIED ELECTRODES

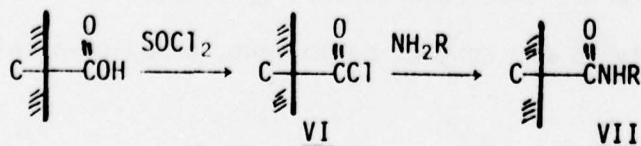
Procedures for immobilizing reagents on electrodes have been devised at a steady pace, and now include several types of covalent bonding between reagent and electrode, coating the electrode with an insoluble variant of the reagent, and chemisorption. Covalent immobilization is tolerant of exposure to different solvents and can be effected on metal oxide and carbon electrodes.

Metal oxide surfaces. SnO_2 ^{1,11}, RuO_4 ^{11c,d;12}, TiO_2 ^{6,11a,c;13}, Pt/PtO ^{3,4,6,11c-e;12b,14}, Au/Au(oxide) ^{14b,d}, Si/Si(oxide) ¹⁵, and Ge ¹⁶ electrodes¹⁷ can be functionalized with a variety of organosilanes, including alkylamine(I,III) acid chloride(IV), and pyridine(V) silanes.



These surfaces can be coupled variously as amides^{4,11d,w;12a}, sulfonamides^{11e}, quaternized^{11a}, and coordinated to metals³. Silanization is, thus, a versatile covalent immobilization strategy. Figure 2 illustrates the cyclic voltammetry of molecules (Structures 1-6) we have immobilized as amides of I on Pt/PtO ¹⁸; note that the silanization chemistry accommodates a wide span of potentials (ca. 2.5 volt) of surface redox structures.

Oxidized sites on carbon surfaces. The carboxylic acid functions on edge planes¹⁹ of graphitic carbon generated by thermal²⁰ or O_2 plasma oxidation²¹ can be coupled with amines or alcohols after activation with thionyl chloride²⁰ or acetyl chloride^{7c}.



(4)

Reaction 4 has been used to prepare a chiral electrode surface²⁰ and to immobilize tetra(aminophenyl)porphyrin^{22,23} and a pyridine ligand²⁴. The immobilized porphyrin (Figure 2, Structure 8) can be metallated^{7c,22} with Co, Mn, Cu, Ni, Zn or Fe. Carbon surface hydroxyl groups can be activated for coupling reactions with²⁵ cyanuric chloride; this promises to have a useful range of reactivity. Carbon surface quinone reacts with nitrophenylhydrazine to form a phenylhydrazone²⁶.

Oxide-free carbon. Mazur²⁷, reasoning that vacuum pyrolysis of carbon surface oxides should create usefully reactive surfaces, demonstrated coupling of olefins to "oxide-free" carbon. Improved coupling yields of reagents with "oxide-free" carbon were subsequently demonstrated with Ar plasma²⁸ and mechanical abrasion²⁹ procedures for removing the oxides. Vinylpyridine, subsequently coordinated to ruthenium^{30a}, is represented in Figure 2 (Structure 7) as a cycloaddition product of the abrasion approach, although the true chemical nature of "oxide-free" carbon surface coupling products remains to be adequately illuminated.

Chemisorption. Chemisorption (or "irreversible" adsorption) is a less controlled approach. Nonetheless, interesting immobilization chemistry is accessible, as shown by Hubbard⁵ in a pioneering study of functionalized olefin chemisorption on Pt, and later work with Π -system reagents on Pt³¹, basal plane pyrolytic graphite^{7f,g,j;32}, and Pt/PtO^{14a}. The Π -system-graphite chemisorption tends to be impermanent when the immobilized reagent is soluble in the contacting solvent.

Redox polymers. If the reagent of interest is incorporated into a polymeric matrix, the equivalent of many monolayers (10-1,000) of reagent can be immobilized. The polymer adheres to the electrode surface by some combination of adsorption and low solubility in the contacting solvent, or by covalent bond-

ing. Polymers have been coated on electrodes by dip^{7e,33} and spin coating^{6,34}, organosilane bonding^{11f,w;14a,c}, electrochemical precipitation³⁵ and polymerization^{30b,36}, adsorption from solutions³⁷, and plasma discharge polymerization^{29,38,39}. Polyvinylferrocene, polyvinylpyridine/ruthenium complex, and polynitrostyrene are examples of these redox polymers.

Polymer coatings have been appealing on several accounts. First, immobilization experiments are technically less demanding than working with monolayers. Secondly, electrochemical responses are larger (since multiple layers of redox sites react). Thirdly, it has been supposed that improved stability results from incorporating reagents into polymers. A polymer framework may however be highly stable while an electrochemically reactive moiety attached to it is no more stable than when immobilized as a non-polymer monolayer. Finally, a theoretical model⁴⁰ for electrocatalysis at modified electrodes has suggested that multilayers are best. The assumptions in this model are not adequately tested. These questions are being addressed in several laboratories and doubtless will soon be answered.

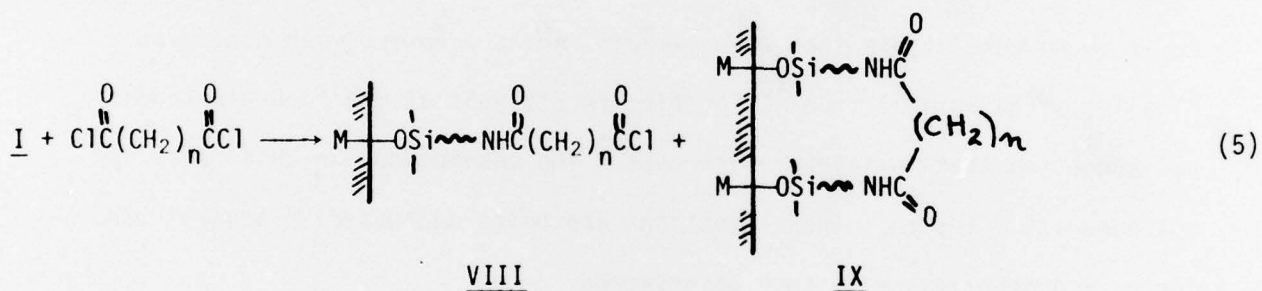
The business of immobilizing molecules on electrodes, while not a mature science, is well advanced. It clearly is possible to rationally select target molecules for electrode immobilization, which is important in designed applications of modified electrodes. Emphasis in the field is gradually shifting to applications.

ANALYSIS OF SURFACE POPULATION AND STRUCTURE

Since immobilization of a reagent tends to fix the microenvironment of its electron transfer reactions, we have stressed analytical characterization of bonded layers. For example, in Reactions 1 and 2, ideally we should determine yields of these surface reactions, and should assess structural, spatial, and dynamic relationships of I and II to the -MOSi- plane and to

their neighbors. These are not easy tasks.

X-ray photoelectron spectroscopy (XPS) has been informative in tracking surface reactions. Figure 3 illustrates how XPS follows Reaction I and a subsequent amidization building up an electrochemically active surface^{4,12a}. Appearance of surface elements is a simple qualitative diagnostic, and from relative peak intensities the layer thickness^{2,41} and N/Si surface atom ratio can be measured^{11c}. The amidization reaction yield, obtained from the N 1s peaks in Curve G, demonstrated that the γ -amine site on I has low reactivity while the terminal amine reacts readily. XPS also allows probing^{11h} of amine site spacing using the bifunctional coupling reaction



Relative populations of VIII and IX assayed as a function of n show that bifunctional coupling (IX) is possible if n is such that the reagent can accommodate to an amine N-N spacing of 4-8 Å.

XPS has also been useful to study Reaction 4 and establish a connection between graphitic edges and reactive carboxylic acid sites⁴². XPS shows that tetra(p-aminophenyl)porphyrin in Reaction 4 forms^{22b}, on the average, two surface amide bonds; the more probable (α,β) of the two possible surface isomers is shown in Figure 2. The α,δ isomer would have a "face-to-face" electrode-ring cavity.

Coverages of electroactive silane-bonded reagents (Figure 2), determined by cyclic voltammetry, are most commonly 0.8 to 4×10^{-10} mole/cm.² and, in

comparisons to expected molecular sizes, approximate non-compacted monolayers. The 0.4×10^{-10} mole/cm.² coverage of Structure 5 for example, is much less than the value for a (Langmuir trough) oriented monolayer of the carboxylic acid of this substance. Coverages by the ruthenium complex³ II are closer to monolayer models. The coverage data, in general, suggest loosely organized monomolecular surface structures with consequent thermal motional freedom and interfacial fluidity, supporting our "floppy molecule" model for electron transfer discussed below.

In occasional samples and under certain reaction conditions, (Structure 4), and especially with chlorosilanes, larger coverages are obtained in silane bonding reactions, suggesting siloxane polymer formation. Coverages usually amount to only ca. 3 - 6 monolayers although thicker layers have been observed 11f;14c,d. Such results suggest that even for samples with average coverage in the monolayer range, some dimer, trimer, etc., sites probably are scattered among the monomer monolayer (I) population. Siloxane polymer globule formation⁴³ is on the other hand avoidable with proper reaction conditions.

Numerous analytical challenges remain, for silane-bonding as well as other modification schemes. In addition to more detailed surface structure evidence, the surface dynamic inferences obtained from electrochemical measurements (see below) need verification from other methods. Polymer-coated electrodes pose special analytical problems, ranging from physical topology of thickly coated surfaces¹⁰ to spatial uniformity of subsequently metallated ones^{37a} to the detailed chemical nature of plasma generated films^{38,39}.

IMMOBILIZED ELECTRON TRANSFER COUPLES SWAPPING ELECTRONS WITH THE ELECTRODE

The report by Moses^{11a} of an electrochemically reactive silane-immobilized compound, methylpyridinium, was quickly followed by additional²⁶ and more reversibly stable examples on carbon^{22a}, RuO₂^{12a}, and Pt/PtO₄⁴. Today electrochemistry of many immobilized electron transfer couples has been

described, including nitroaromatics^{4,6,7e,11f,12a}, iron-sulfur clusters^{11u}, pyrazolines^{10,11p,q}, ferrocenes^{11d,w;14,15,25a,29,31,35,36b,39}, ruthenium complexes^{3,7i,24,28,32a,37}, tetrathiafulvalene^{12c}, viologens^{25d}, porphyrins^{7c,i,j,l;22}, quinones^{7b,g;27,32b}, and *o*-tolidine^{25c}. The emphasis has been on simple and stable oxidized and reduced forms, and the electron transfer chemistry is thus mostly one electron outer sphere.

We have shown that ^{the} formal potential, $E_{\text{surf}}^{\circ'}$, of an immobilized electron transfer couple (Figure 1), is nearly the same as that of its unattached, structural analog, $E_{\text{soln}}^{\circ'}$, and not perceptibly sensitive to electrode material or immobilization chemistry. One readily calculates that 2×10^{-10} mole/cm.² of a molecule tethered by a 10 Å chain corresponds to a 2 M "volume concentration", large enough to depress the concentration of interfacial solvent, and to potentiate substantial activity effects. The data indicate that the next effects on the free energy difference of oxidized and reduced forms are fairly small for the cases studied.

Surface activities do manifest themselves in the broadness (E_{FWHM}) of cyclic voltammetric peaks^{32b}. $E_{\text{FWHM}} = 90.6$ m.v. for surface activity proportional to coverage⁵, but an exponential relation with "repulsive" activity parameters^{32b,44} predicts broadened surface peaks. $E_{\text{FWHM}} > 90.6$ m.v. is an almost universal effect observed to date⁴⁵. Surface structural heterogeneity may also contribute to peak broadening^{11d,22b}, complicating analysis of the problem.

A crucial observation is that electron transfer couples exhibit electrochemical reactivity irrespective of how they are immobilized: electronically insulating connecting chains^{11a} as in the organosilanes, or carefully chosen conjugated connections^{25a,32a}, or in polymeric multilayers^{7e,14b,14c}. For II-system molecules chemisorbed on pyrolytic graphite^{7f}, close contact

makes the electron transfer process easy to visualize, and the collision number (frequency factor) for electron transfer is conceivably as large as kT/h (ca. $6 \times 10^{12} \text{ sec}^{-1}$). Anson⁴⁶ has reasoned that, given equal electron transfer energy barriers for attached and unattached reagents, this frequency term could provoke larger electron transfer rates for the former. Indeed, except where a proton transfer step intervened, electron transfer rates for graphite-adsorbed reactants proved immeasurably fast and only a lower limit (ca. 10^4 sec^{-1}) could be placed on the rate constant.

When the electron transfer couple is on the other hand immobilized via some connecting molecular bridge, or is distributed throughout a polymer lattice, short range motions of the redox site may become important. In this view, recognizing the combination of connecting chain flexibility and coverage-suggested layer non-compactness in organosilane-bound monolayers, we proposed^{11a,c} that "floppy" chain folding of the surface structures would be associated with electron transfer as illustrated in Figure 4. The average distance for electron transfer is unknown and possibly more separated from the conducting electrode material than for an unattached reactant. The time-average electrode-reactant separation depends on the distribution of structural conformations as influenced by coulombic terms (e.g., electrode vs. reactant charge), from the electrode side⁴⁷, and solvation effects^{14a} (e.g., relative solvation of reactant, connecting chain, and electrode), from the solution side. In some instances the average conformation might be folded and floppiness unnecessary, for electron transfer; in others lateral electron transfer events (Figure 4) could be an important accessory mode of reaction^{11c}.

The collision frequency of a reactant tethered to an electrode by a chain of length d can be approximated as $A = 4D'/d^2 \text{ sec}^{-1}$ where D' is a transport parameter. If chain-folding energy barriers are comparable to barriers for molecules diffusing in solutions, D' is comparable to a diffusion

coefficient. For ferrocenes 3 and 5 in Figure 2, assuming $D' \sim 10^{-6} \text{ cm}^2/\text{sec}$, $A = 2 \times 10^8$ and $2 \times 10^7 \text{ sec}^{-1}$. These are much smaller collision frequencies than estimated by Anson⁴⁶ but as mass transport factors remain too fast to be limiting even during fast (ca. 10^{-2} sec) voltammetric scans⁴⁸.

The transport of electrochemical charge through multilayers of electron transfer sites, as in redox polymers, is more complex than the monolayer situation, but is slower and more amenable to study. Polymer coated electrodes bear large coverages of immobilized electron transfer couples, $10^{-9} - 10^{-6} \text{ mole/cm}^2$ and often exhibit cyclic voltammetric waveshapes^{7e,10,11w,14c,d;29,35,39} indicative of slow electrolysis of the surface film. Conceptually, it seems likely that electron hopping between adjacent localized oxidation states will be a mechanism for the migration of charge through a fixed site polymer matrix. That migration of charge in redox polymers / can obey Fick's Laws has been observed³⁹. What controls the rate of the migration, whether site-site collision², counterion mobility^{37b}, solvent swelling^{39c}, or polymer chain deformations^{39b}, for any given redox polymer, or in general, is at present an unsettled matter. These issues must be understood over a range of redox polymers before systematic application can be made to electrocatalysis, photoelectrocatalysis, and analysis.

CHEMICAL REACTIONS OF ATTACHED REAGENTS

Assuming that the initially immobilized (resting) oxidation state of an electron transfer couple is stable, we are particularly interested in any chemical reactivity (or stability) incited by electrochemical change of oxidation state, since this determines usefulness in applications. Instability as reflected in decay of the electrochemical response of an immobilized electron transfer couple can arise by reaction of the non-resting oxidation state, by reaction attendant to electron transfer itself, or by potential-dependent phenomena such as electrode corrosion and reactions of the immobilizing bonds. For organosilane based immobilization it has been established in several

cases^{4,12a,21a} that stability is dictated by reactivity of the electron transfer couple not the silane-electrode bonding. Specifically, decay of the wave for ferrocene 4 in Figure 2, is associated with the time the electrode spends in the ferricenium state, not the number of electrochemical turnovers between states. This is an important distinction for electrocatalytic applications, and illustrates the inadequacy of characterizing electrode stability by stating a number of usable cycles as is common in the literature.

Whether reactivity is promoted or diminished by immobilization so far varies. As compared to unattached molecular analogs and to polymeric multilayers^{6,7e}, nitroaromatic radical anions are less stable as immobilized monolayers^{4,12a,49}. A dependence on electrode material suggests some specific interaction with the electrode. Decreased stability, as compared to solution analogs, of monolayers of monocyclic pyrazoline radical cations^{11p} and of polypyridine ruthenium(I) complexes³ has also been reported. The rate of nitrile ligand substitution in the Ru(III) state of II is enhanced³, whereas in an attached Ru(III)-EDTA complex, ligand substitution is slowed⁵⁰ by ca. 10^3 . The substantial photolability of II is quenched by its immobilization on Pt, presumably because of proximity to the metal³.

Considering the concentrated nature of bonded monolayers and redox polymers, evidences of intermolecular surface reactions are of interest since collisional frequencies and cross-sections may differ from those in freely diffusing fluids. Detected reactions between monolayer sites include dimerization of a pyrazoline cation radical^{11r}, and disproportionation⁷ⁱ of the Ru(III)-NO₂ complex of 2 of Figure 2. Both reactions were slower than for the unattached versions. Figure 2 illustrates the usefulness of low temperatures to "freeze" disproportionation of attached Ru(III)NO₂; at the temperature used, (-80°C in butyronitrile) the Ru(III) reduction wave persists for many minutes

whereas for an unattached complex it is undetectable at room temperature. In a quantitative kinetic study, Lenhard^{14a} showed that ferrocene 4, Figure 2, decays by a rate law second order in ferricenium, with a rate constant of $7 \pm 3 \times 10^5 \text{ cm}^2/\text{mole-sec}$. Although the reaction could be followed over several half-lives, the eventual breakdown of the second order rate law anticipated if ferricenium-ferricenium collisions are involved was not reached.

Electrocatalytic reactions (Reaction 3) is an important designed application of modified electrodes. Examples of electrocatalysis so far reported include ascorbic acid oxidation by attached benzidine^{7a}, NADH^+ oxidation by 3,4-dihydroxybenzylamine^{7b}, and O_2 reduction by Fe tetra(p-aminophenyl)porphyrin^{7c}, all amide coupled to carbon as in Reaction 4, ascorbic acid^{7a} and NADH^+ ^{7d} oxidation by carbon surface oxides, CCl_4 and O_2 reduction by poly(p-nitro-styrene) dip coated on Pt^{7e}, O_2 reduction by Fe protoporphyrin IX^{7f}, Co tetrasulfonatephthalocyanine^{7g}, and a cofacial dicobalt porphyrin dimer^{7h}, all chemisorbed on basal plane pyrolytic graphite, O_2 reduction by Co tetrapyrrolylporphyrin adsorbed on glassy carbon^{7j}, and tri(chlorophenyl)phosphine oxidation⁷ⁱ by the Ru(III)NO_2 complex 2 of Figure 2. The detail in mechanistic and product identification known for these examples varies substantially, as does the turnover stability of the surface couple. In no case has an adequate quantitative kinetic analysis been developed. In qualitative terms, the most spectacularly successful modified electrode electrocatalysis has been the four electron, mass transfer controlled reduction of O_2 to H_2O without significant H_2O_2 production^{7h}. This elegant electrocatalytic reaction is based on the concept of dual binding/^{and} electron transfer to O_2 from the faces of a porphyrin dimer, the spacing between which is critical.

Non-catalytic forms of reactivity of the electron transfer reagent where the product remains electroactive and attached to the electrode include

reversible proton^{7f} and ligand^{22b,51} transfer closely associated with electron transfer, and certain protonations^{7c,i} and ligand substitutions³. Such reactions are of interest by probing immobilized reagent chemistry for comparison to familiar solution events.

Photoinitiated reactivity of immobilized molecules is also of interest. On illuminated (n-type) semiconductor electrodes, the immobilized chromophore acts, in photosensitization^{8,11i,j,m;52,53} as an excited state reductant, irreversibly injecting an electron into the conduction band, and in bandgap absorption, as a ground state reactant, neutralizing a valence band hole (anti-photocorrosion⁹). Both schemes depend on efficient reduction of the resulting oxidized surface reagent by some consumable solution substrate in a cycle analogous to Reaction 3, which is central to both electrocatalytic and photo-electrochemical applications.

ELECTROCHEMISTRY OF UNATTACHED REACTANTS AT MODIFIED ELECTRODES

Electron transfer reactions of unattached substances (typically stable one-electron types) at non-mediating monolayer and multilayer modified surfaces are useful probes of interfacial structure. Silane bonded^{2,4,11c,q} and chemisorbed^{7f,47} monolayers on electrodes in most cases retard the reaction rate of dissolved reactants, although exceptions exist^{2,7f,11q,47}. The expected effects are (i) enhancement of current density at accessible surface sites (sites of bonding being considered inaccessible), (ii) steric barriers to such access, and (iii) (for charged attached molecules) changes in the interfacial potential distribution altering the potential experienced by the solution reactant at its distance of closest approach (ϕ_2 effect)⁵⁴. The ϕ_2 factor for bonded cationic molecules retards the electron transfer rate of cationic solution reactants, and enhances that of anionic reactants. Such effects have been observed for both silane-bonded² and chemisorbed⁴⁷

cationic layers, and an elegant theoretical analysis was carried out for the latter. The enhancement of current density effect applies to any solution reactant and will be most noticeable for reactants with slow electron transfers (at naked electrodes). Sterically impeded access of solution reactants (by the bonded reagent) to open sites is, strictly speaking, a mass transport effect, but over monolayer distances such kinetics become incorporated with those of electron transfer. Attempts to demonstrate steric effects by study of a given solution reactant at a series of surfaces with successively more bulky bonded organosilanes^{11q} are unfortunately compromised by uncertainty whether organosilane coverage remains constant in the series.

Coatings of non-mediating multilayers (polymers) on electrodes pose a greater likelihood of access limitations on unattached reactants, which may not be able to cross (dissolve in) the polymer film. Since the distances are greater, access kinetics are more readily associated with mass transport. This point has relevance to electrocatalysis theory⁴⁰ where a questionable assumption of uniform access to all polymer sites was made. Although investigations have only recently begun, examples of retardation of electrochemical rates have been encountered^{7e,11c,14e,33,38,39} and again exceptions^{11c,11w,39}. Important factors can be expected to include reactant size and charge, solvent swelling and counterion penetration (degree and rate) into the film and pinholes and channels. Solvent swelling, normally greater for polymers bearing fixed charged sites, is important in permitting access of electrolyte into the film, without which either a large uncompensatable resistance effect is experienced^{7e}, or by adequate "dry" electronic conductivity the film becomes an extension of the electrode material with electron transfer occurring at its solution interface^{34a,38}. With charged polymer films, penetration of

neutral reactants or reactants of opposite charge to the fixed sites is much more facile than penetration of reactants of like charge, due to Donnan exclusion, as observed with a siloxane polymer version of I under conditions protonating the amine sites^{11c}. The role of solvent swelling is illustrated^{39c} with plasma polymerized vinylferrocene films, which in CH_3CN (swells the film) permit reactant access, but in water (non-swelling) act as a barrier.

THE NEAR FUTURE

Given the many excellent research programs attracted by the tailormade appeal of chemically modified surfaces, the chemical diversity and applications of decorated electrodes are likely to grow for some time. In particular, electrocatalytic, photoeffect, and electrochromic phenomena at modified electrodes will be intensely scrutinized applications some of which will translate into far future technology. Selective analysis is a hardly broached but pregnant applications area. An enormous potential remains for using modified surfaces as fundamental probes of transient interfacial charge transfer and transport events. The depth of our achievable insights into such events is fettered by ignorance about details of attached molecules' spatial distribution and dynamics and more useful probes of these and of the potential distribution at the electrode need invention. Finally, study of polymer-coated electrodes is likely to lead to significant contributions to the physical chemistry of polymers.

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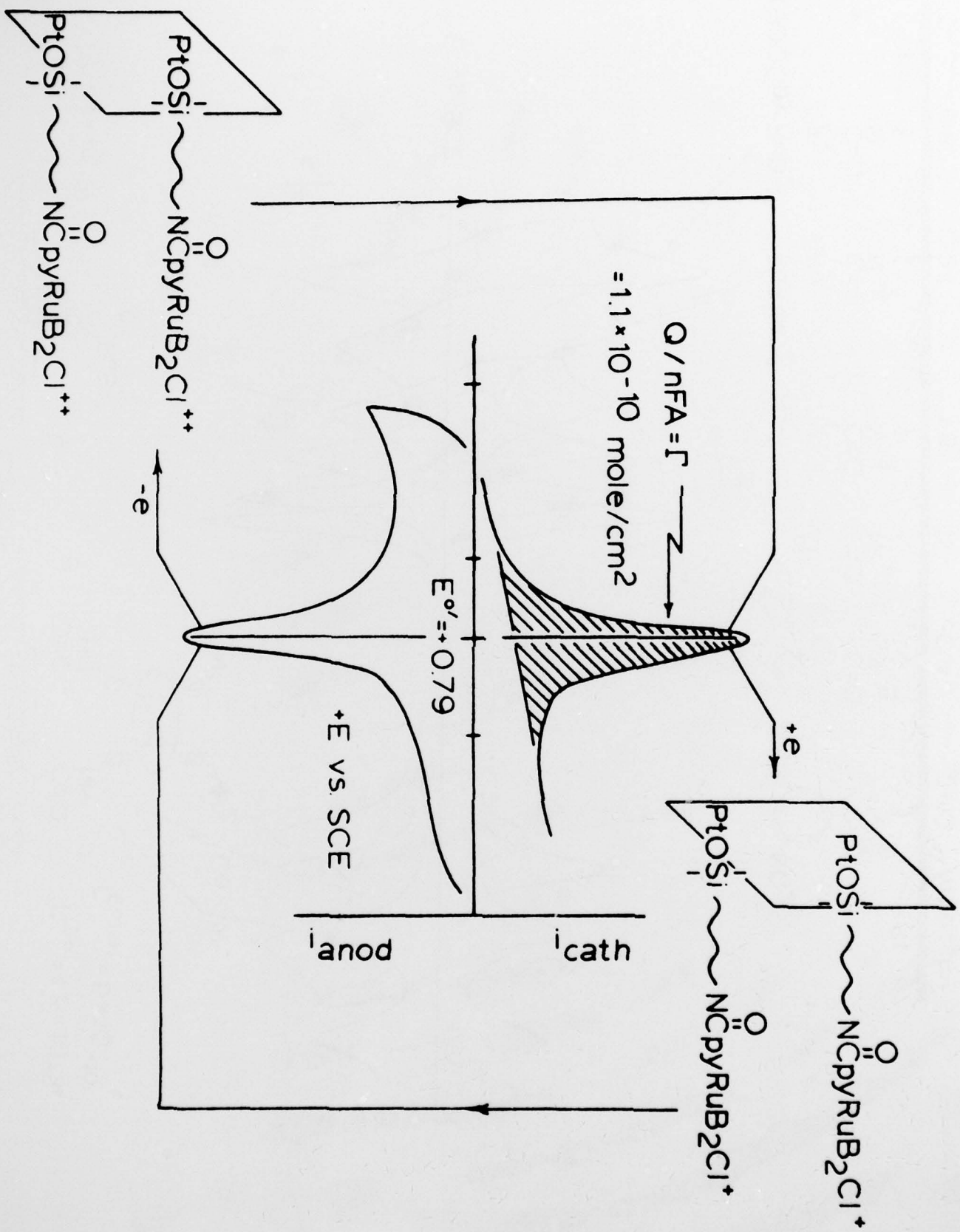
FIGURE LEGENDS

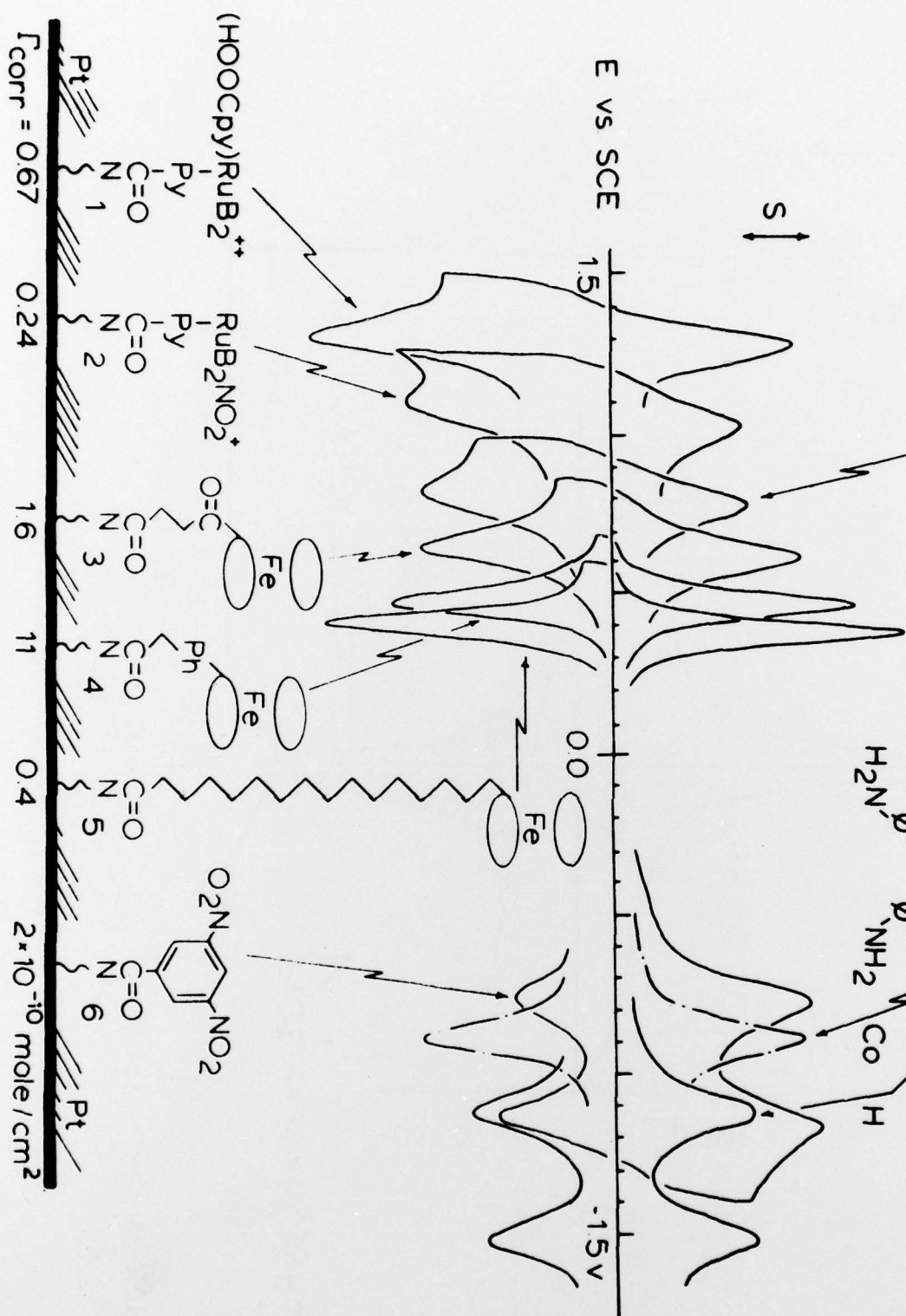
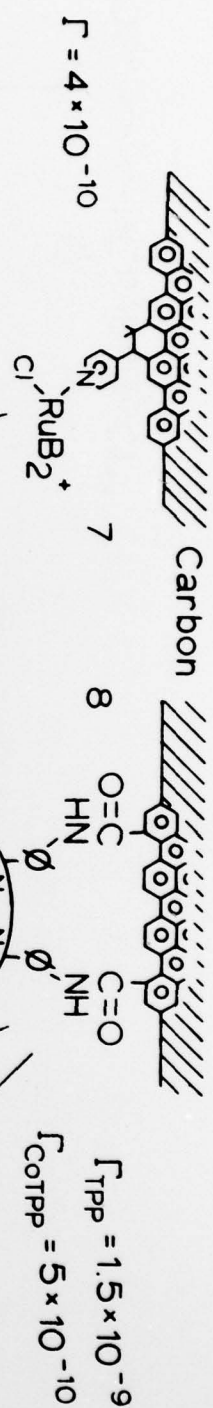
Figure 1. Cyclic voltammetry (0.2 volt/sec. triangular potential sweep) of (iso-nicotinic acid) Ru^{II} (2,2'-bipyridine) Cl^+ attached to Pt/PtO surface as in Reaction 2. $\text{CH}_3\text{CN}/\text{Et}_4\text{NClO}_4$.

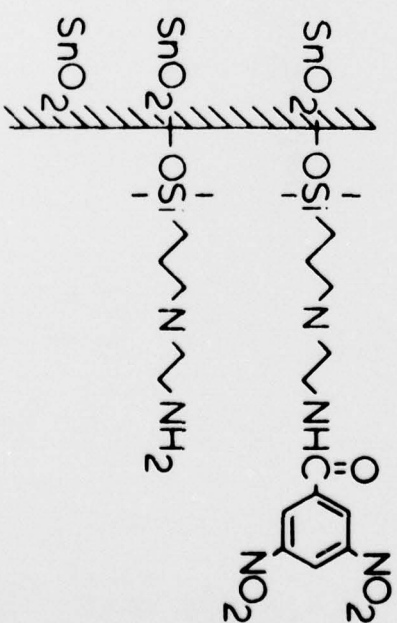
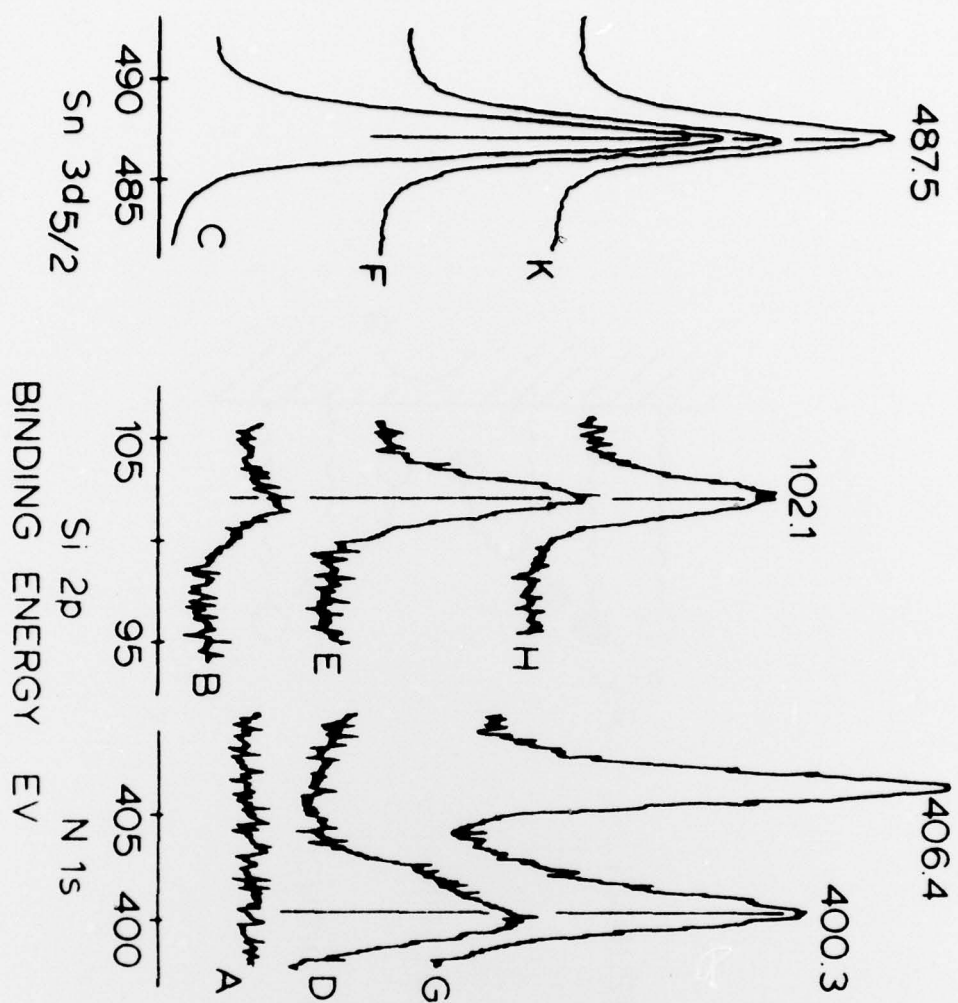
Figure 2. Cyclic voltammograms of selected modified electrode surface structures. Structures 1-6 are all coupled to Pt/PtO by chemistry as in Reaction 2; B is 2,2'-bipyridyl; Structures 3-5 are ferrocenes. Structure 7 is made by abrading glassy carbon in the presence of vinylpyridine followed by reaction with a solution of RuB_2 (dimethoxyethane) $^{2+}$ containing chloride. Structure 8 is the α,β surface isomer for tetra(p-aminophenyl)porphyrin reacted as in Reaction 4 and metallated with a solution of CoCl_2 . Cyclic voltammograms at positive E are in CH_3CN , those at negative E are in DMSO. Structure/current sensitivity(S)/scan rates are: 1/ $6\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 2/ $3\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 3/ $11\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 4/ $70\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 5/ $3\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 6/ $12\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 7/ $16\mu\text{A cm}^{-2}/0.2 \text{ v/s}$; 8 (unmetallated)/ $55\mu\text{A cm}^{-2}/0.1 \text{ v/s}$; 8 (cobalt)/ $14\mu\text{A cm}^{-2}/0.1 \text{ v/s}$.

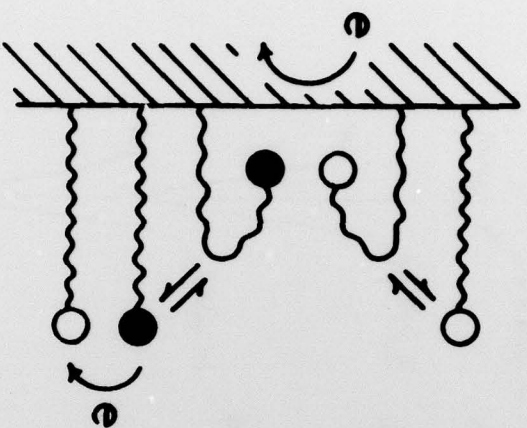
Figure 3. X-ray photoelectron spectroscopy of a native film of SnO_2 on glass (Curves A-C), after silanization with en silane (Curves D-F), and after further amide coupling with 2,4-dinitrobenzoyl chloride (Curves G-K).

Figure 4. Schematic view of electron transfer reactions of oxidized (\circ) and reduced (\bullet) moieties on monolayer electrode surfaces.









chain folding

electron transfer

lateral electron transfer